SHORT PAPERS

THE PRESENCE OF DIMETHYL- AND DIETHYL-NITROSAMINES IN DEIONIZED WATER

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Summary—Twenty seven of 42 samples of water exposed to deionizing resins contained from 0·03 to 0·34 ppb (μg litre) dimethylnitrosamine, as determined by gas–liquid chromatography combined with thermal energy analysis, a detection method claimed to be specific for nitrosamines. Twelve of these 27 samples, mainly from water obtained after resin regeneration, were confirmed as containing dimethylnitrosamine by gas–liquid chromatography–high resolution mass spectrometry. Two samples of water deionized at the Center, were confirmed as containing 0·33 and 0·83 diethylnitrosamine as well as the dimethylnitrosamine. The origin of these nitrosamines is unknown at present.

Introduction

Our confirmation of the presence of 3–5 ppb dimethylnitrosamine (DMNA) in fried bacon made with or without the addition of low concentrations of nitrite (Fiddler, Pensabene, Podebradsky, Doerr & Wasserman, 1975) prompted an extensive investigation of the source of the nitrosamine (NA) in this product. Each of the chemicals and reagents used in the analytical procedure was examined. Deionized water was one of the materials tested, and with the gas–liquid chromatography (GLC)-alkali flame ionization detector (AFID) NAs were not detected. The same reagent components were then re-evaluated using a Thermal Energy Analyser (TEA). This detector is extremely sensitive and is claimed to be specific for nitrosamines (Fine, Rufeh & Gunther, 1973). The application of the GLC–TEA to the detection of apparent NAs in deionized water is described and the results are given below.

Experimental

Water (1·2 litre) was extracted twice with 400-ml portions of methylene chloride; the extracts were combined, dried by passage through anhydrous sodium sulphate and concentrated to 1·0 ml. After quantification by GLC using the TEA detector, the extracts were concentrated to about 0·1 ml for GLC–mass spectrometric (MS) confirmation. The operating conditions for the TEA are similar to those described by Fine & Roundbehler (1975) and Fine, Rufeh, Lieb & Rounbehler (1975). A 5 μl injection of 0·6 ng NA could easily be detected. This was equivalent to 0·01 ppb (μg/litre) with respect to the original water sample. Recovery of 250 ng DMNA added to 1·2 litre of distilled water was consistently in excess of 90%.

DMNA and diethylnitrosamine (DENA) were confirmed by matching the GLC retention times with those of the known NAs by peak-matching the exact mass of the parent ions *m/e* 74·0480 and 102·0723, respectively. The GLC–MS conditions have been published elsewhere (Kushnir, Feinberg, Pensabene, Piotrowski, Fiddler & Wasserman, 1975; Pensabene, Fiddler, Gates, Fagan & Wasserman, 1974). Approximately 3 ng NA/μl injection were needed for MS confirmation. Nitrosamines are potentially carcinogenic and these compounds should be handled with care.

Results and Discussion

Sixty-two samples of water were analysed for NAs. The results are presented in Table 1 and a typical TEA chromatogram is shown in Fig. 1. Volatile NAs were not detected in distilled water or concentrates of methylene chloride solvent. Of the 20 samples of non-deionized water tested, 0·01 ppb apparent DMNA was detected in two samples and 0·05 ppb DENA was detected in a third sample obtained from a tap at the Center, delivering the municipal water supply. Eleven of 14 samples of Center-deionized water had TEA-detectable levels of apparent NAs. Two of these samples were confirmed by MS as containing 0·15 and 0·20 ppb DMNA and 0·33 and 0·83 ppb DENA. Center water examined immediately after it had passed through exhausted resin contained 0·12 ppb DMNA which was confirmed in one of seven samples tested. However, after the resin was regenerated, 13 of 19 samples contained detectable quantities of DMNA (0·03–0·34 ppb). Of these, ten were confirmed by MS. The Center demineralizer was of the mixed-bed type containing strong anion and cation resins. DMNA was also detected, but not confirmed, in both water samples obtained from a different demineralizing system located in the Center pilot plant. This was a two-bed system containing strong cation and intermediate strength anion resins.

Samples of water were taken from five locations at which water from the Center demineralizer had

*Agricultural Research Service, US Department of Agriculture. Reference to a particular brand or firm name does not constitute an endorsement by the US Department of Agriculture over similar products not mentioned.

Table 1. *Nitrosamines in deionized water*

Type of water sample	Analytical method	No. of samples in which DMNA was detected total no. of samples	Level of DMNA detected (ppb)	No. of samples in which DENA was detected total no. of samples	Level of DENA detected (ppb)
Non-deionized	GLC–TEA	2/20	0·01	1/20	0·05
Deionized at the Center	GLC–TEA	11/14	0·05–0·20	2/14	0·33, 0·83
	GLC–MS*	2/11	0·15, 0·20	2/2	0·33 0·83
Deionized at the Center, using (a) exhausted resin	GLC–TEA	1/7	0·12	0/7	ND
	GLC–MS*	1/1	0·12		
(b) regenerated resin	GLC–TEA	13/19	0·03–0·34	0/19	ND
	GLC–MS*	10/13	0·08–0·34		
Deionized in a pilot plant at the Center	GLC–TEA	2/2	0·03, 0·05	0/2	ND

ppb = μg/litre ND = Not detected

*GLC–high-resolution MS was used for confirmation of GLC–TEA results indicating the presence of DMNA/DENA.

passed through further individual deionizing cartridges making the water double-deionized. Seven of 12 water samples thus treated apparently contained 0·03 to 0·31 ppb DMNA, but this was not confirmed by MS because relatively small quantities of water had been extracted, leaving insufficient NA for MS. The cartridges were removed and examined for residual NAs by extracting the resin with methylene chloride. The resin in four of the six cartridges tested contained detectable quantities of DMNA. Two of these were confirmed by MS at concentrations of 1·6 and 23 ppb DMNA based on moist resin.

A number of samples containing concentrations of DMNA insufficient for MS confirmation had a peak with the same retention time as authentic DMNA on three different GLC columns (a 15% Carbowax 20 M-TPA on 60/80 Gas Chrom P in a Varian Aerograph 2700 gas chromatograph interfaced with the TEA, a 6% Silar 10 C on 60/80 Gas Chrom P in a Perkin Elmer 3920, and a Chromosorb P in a Hewlett Packard 5710A). The two latter columns were equipped with N–P or alkali flame ionization detectors. In addition, methylene chloride extracts of several samples containing trace concentrations of apparent DMNA were treated with HBr in glacial acetic acid or transferred into aqueous solutions and exposed to ultraviolet light (365 nm). When the samples were rechecked by GLC–TEA, no apparent NA was present. Both of these treatments are known to cleave the N–NO group of nitrosamines (Eisenbrand & Preussmann, 1970; Sander, 1967). Thus, all available evidence suggests that DMNA was present.

Although 0·03–0·20 ppb DMNA was found in the deionized water at the Center, only the higher level could have made a significant contribution to the low levels of this NA detected and confirmed in occasional samples of bacon prepared without nitrite. Since the water was used to prepare some analytical reagents, sufficient DMNA could have been added to yield up to 5 ppb with respect to the meat sample. This does not necessarily invalidate data reporting low levels of DMNA and DENA.

Although the concentrations found were very low, we are reporting this finding of NAs in water exposed

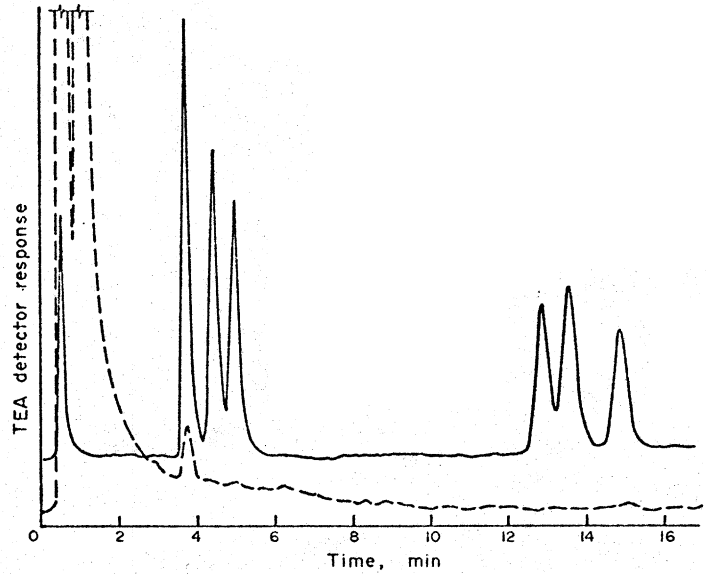

Fig. 1. TEA chromatograms: 2 ng each of standard samples of dimethyl-, methylethyl- and diethylnitrosamine and nitroso derivatives of piperidine, pyrrolidine and morpholine (——); sample of deionized water containing 0·24 ng or 0·03 ppb DMNA (- - -).

to deionizing resins since it has potentially far-reaching implications in areas such as public health, analysis and toxicology. The origin of these NAs is unknown at present and additional investigations are in progress.

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